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**Heat transfer liquids with glass corrosion prevention, in particular for solar plants**

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10 The present invention relates in particular to borate-free concentrates based on glycols with glass corrosion protection for heat transfer liquids, in particular for solar plants, comprising amines and, if required, stabilized silicates and hydrocarbon-thiazoles and hydrocarbon-triazoles; further corrosion inhibitors and other components may also be present. The present invention furthermore relates to ready-to-use aqueous heat transfer liquids which are  
15 based on said concentrates, and their use in solar plants.

Concentrates for heat transfer liquids, in particular for solar plants, generally contain alkylene glycols, especially 1,2-propylene glycol or ethylene glycol, as the main component. For use in solar plants, they are diluted with water and, in addition to preventing freezing,  
20 should ensure good heat transfer. Alkylene glycol/water mixtures are, however, very corrosive at the high temperatures occurring in intense sunlight and in particular those occurring when the plant is not operating; the various metals, for example copper, brass, steel, cast iron (gray cast iron), lead, tin, chromium, zinc, aluminum, magnesium and alloys thereof and solder metals, for example tin solder (soft solder), which in principle can occur  
25 in the heat transfer circulation of solar plants therefore have to be adequately protected from various types of corrosion, for example pitting, crevice corrosion, erosion or cavitation. A large number of individual chemical substances is known from the prior art for use as corrosion inhibitors for metals in such systems.

30 The prior art includes a number of patents and patent applications in which heat transfer liquids for solar plants containing effective corrosion inhibitor formulations for metals are described, some of which are mentioned below.

DE 195 25 090 A1 describes heat transfer liquids for preventing the deposition of solids in  
35 the solar absorbers comprising 1,2-propylene glycol, polyethylene glycol having a molar mass of 400 and water, in which borax, silicate, dicarboxylic acids, sodium benzoate, benzotriazole, tolutriazole, sodium nitrate or sodium nitrite is used as a corrosion inhibitor.

EP 0 971 013 A1 describes aqueous heat transfer media for solar plants, which contain tri- and/or tetraethylene glycol, 1,2-propylene glycol and/or ethylene glycol, comprising a content of borates, silicates, mono- or dicarboxylic acids, sodium benzoate, benzotriazoles, tolutriazoles, nitrites or nitrates as corrosion inhibitors.

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EP 0 109 377 A2 claims a solar collector which contains a heat transfer liquid comprising monoethylene glycol or glycerol, water, formic acid and a quaternary ammonium salt.

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EP 0 092 687 B1 describes an aqueous corrosion-inhibiting heat transfer composition which is also suitable for solar systems and contains an alcohol, for example ethylene glycol or propylene glycol, and an organosiloxane/silicate copolymer and, in the absence of nitrite, contains at least one nitrate salt. Furthermore, known corrosion inhibitors for metals, such as molybdate, borate, phosphate, benzoate, hydroxybenzoate, nitrite, tolutriazole, mercaptobenzothiazole and benzotriazole may be present.

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For solar plants, there are now newer solar collectors comprising special glass, for example comprising special borosilicate glasses, in which the heat transfer liquid no longer flows through metal tubes inside evacuated glass tubes but directly through the glass tubes. The internal surfaces of the glass tubes through which the heat transfer liquids flow can suffer corrosive attack, which leads to opacity and, associated with this, reduced energy absorption from sunlight. The heat transfer liquids of the prior art which are available on the market are still in need of substantial improvement in this respect.

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The problems of glass corrosion are not described and have not been solved to date by the known prior art mentioned above.

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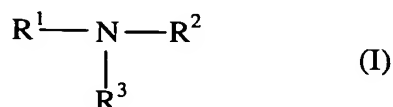
It is an object of the present invention to provide novel concentrates and heat transfer liquids to be prepared therefrom for solar plants. These are intended to be in particular solar plants in which the heat transfer liquid is directly in contact with the glass, for example the glass tubes. The liquids to be provided should no longer have the disadvantages of glass corrosion of the prior art.

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We have found that this object is achieved by heat transfer liquid concentrates with glass corrosion protection, in particular for solar plants, comprising, in addition to at least one glycol,

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- a) from 0.05 to 10, preferably from 0.1 to 5, % by weight, based on the total amount of the concentrate, of one or more aliphatic amines of the general formula (I),



where  $\text{R}^1$  to  $\text{R}^3$  may be identical or different and are hydrogen, straight-chain or branched  $\text{C}_1$ - $\text{C}_9$ -alkyl or  $\text{C}_1$ - $\text{C}_9$ -hydroxyalkyl,

- b) from 0.005 to 3, preferably from 0.01 to 1, % by weight, based on the total amount of the concentrate, of one or more silicates which, if required, have been stabilized,
- c) from 0 to 3, preferably from 0.01 to 3, in particular from 0.05 to 1, % by weight, based on the total amount of the concentrate, of one or more corrosion inhibitors selected from the group consisting of the hydrocarbon-triazoles and the hydrocarbon-thiazoles,
- d) from 0 to 5, preferably from 0.01 to 1, % by weight, based on the total amount of the concentrate, of one or more alkali metal, ammonium or substituted ammonium molybdates and
- e) from 0 to 1, preferably from 0.1 to 0.5, % by weight, based on the total amount of the concentrate, of one or more polymeric hard water stabilizers.

The novel concentrates for heat transfer liquids can be used in conventional solar plants, but in particular in newer systems comprising special glass, in which the heat transfer liquid no longer flows through metal tubes inside evacuated glass tubes but directly through the glass tubes, with the result that particular protection of the internal glass surfaces from opacity due to corrosion is required.

We have found that effective corrosion prevention in solar plants, in particular those with direct contact between the heat transfer liquid and the glass, for example the glass tubes, can be achieved by the combination of the amines used according to the invention with silicates, i.e. the components a) and b).

All amounts stated in the present application relate to the total amount of the concentrate.

In a preferred embodiment,  $R^1$  to  $R^3$  are selected from hydrogen, alkyl radicals with 2 to 9 carbon atoms and alkyl radicals with 1 to 9 carbon atoms which have one or more hydroxyl substituents. In particular,  $R^1$  to  $R^3$  are selected from hydrogen and alkyl groups with 3 or 4 carbon atoms and alkyl radicals with 3 or 4 carbon atoms which have one or more hydroxyl substituents.

Examples of preferred amines are ethylamine, propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, tert-butylamine, n-butylamine, n-pentylamine, n-hexylamine, n-heptylamine, n-octylamine, isononylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, diisobutylamine, triethylamine, diisopropylamine, butyldiethanolamine and mono-, di- and triethanolamine.

For the purposes of the present invention, alkyl-substituted amines in which at least one alkyl radical carries at least one hydroxyl substituent are particularly preferred.

Diisopropanolamine or butyldiethanolamine is particularly preferably used for component a).

In a further preferred embodiment, the component b) contains at least one alkali metal silicate, particularly suitable silicates being those described in EP-A 0 189 527. Examples are alkali metal orthosilicates, alkali metal metasilicates, alkali metal tetrasilicates and alkali metal silicates. The sodium salts are preferred. In particular, sodium metasilicate is used.

The alkali metal silicate is furthermore preferably stabilized by conventional organosilicophosphonates, for example according to EP-A 0 189 527 or DE-OS 29 12 430, or conventional organosilicosulfonates, for example according to EP-A 0 061 694, in conventional amounts. Silicates stabilized by organosilicophosphonates are particularly preferred.

The organosilicophosphonates disclosed in EP-A 0 189 527 and DE-OS 29 12 430 and the organosilicosulfonates disclosed in EP-A 0 061 694 are an important component of the present invention and are hereby incorporated by reference in the present Application.

In a further preferred embodiment, the component c) is a mixture of at least two hydrocarbon-thiazoles, a mixture of at least one hydrocarbon-triazole and one hydrocarbon-thiazole or a mixture of at least two different hydrocarbon-thiazoles. Examples of preferred hydrocarbon-thiazoles are benzothiazole and 2-mercaptobenzothiazole.

A mixture of at least two different hydrocarbon-triazoles is preferably used. These are selected in particular from benzotriazole, toluotriazole and 1H-1,2,4-triazole.

In a further preferred embodiment, the component d) contains sodium molybdate, in particular sodium molybdate dihydrate.

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In a further preferred embodiment, the component d) contains at least one hard water stabilizer based on polyacrylic acid, polymaleic acid, acrylic acid/maleic acid copolymers, polyvinylpyrrolidone, polyvinylimidazole, vinylpyrrolidone/vinylimidazole copolymers and copolymers of unsaturated carboxylic acids and olefins.

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In addition to said inhibitor components, for example, soluble magnesium salts of organic acids, preferably magnesium benzenesulfonate, magnesium methanesulfonate, magnesium acetate or magnesium propionate, and furthermore hydrocarbazoles and/or quaternized imidazoles, as described in DE-A 196 05 509, in conventional amounts may also be used as further inhibitors.

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The pH of the novel heat transfer concentrates is usually from 6 to 11, preferably from 7 to 10, in particular from 7.5 to 10. The desired pH is established, as a rule, by adding alkali metal hydroxide to the formulation. Solid sodium hydroxide or potassium hydroxide and aqueous sodium hydroxide solution and potassium hydroxide solution are particularly suitable for establishing the pH.

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The novel concentrates contain no borate. For the purposes of the present invention, borate may be present in the heat transfer liquids or concentrates, but then the advantages according to the invention are not achieved in most cases. In particular, in the presence of strongly alkaline borates, greater glass corrosion is generally to be found, which can assume substantial levels depending on the composition of the liquid. The borate usually used is borax (sodium tetraborate).

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The novel heat transfer liquid concentrates preferably furthermore contain a freezing point depressant which is selected from alkylene glycols and derivatives thereof. The freezing point depressant is preferably present in the novel concentrates in an amount of at least 75, more preferably at least 85, % by weight.

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First, lower alkylene glycols and derivatives thereof, for example ethylene glycol and 1,2-propylene glycol, are suitable for use in the novel concentrates. However, higher glycols and glycol ethers are also suitable, for example diethylene glycol, dipropylene glycol, tri-

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and tetraethylene glycol, polyethylene glycol, monoethers of glycols, for example the methyl, ethyl, propyl and butyl ethers of ethylene glycol, propylene glycol, diethylene glycol and dipropylene glycol. 1,3-Propanediol and glycerol are furthermore suitable. A single solvent or a mixture of two or more solvents may be used.

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Ethylene glycol and/or 1,2-propylene glycol are preferably used, in particular 1,2-propylene glycol.

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In a preferred embodiment, the freezing point depressant is based on 1,2-propylene glycol or mixtures thereof with other polyalcohols, at least 85, preferably 90, % by weight of 1,2-propylene glycol being present in the mixture.

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The novel heat transfer concentrates may also contain, in conventional small amounts, antifoams, preferably in amounts of from 0.003 to 0.008% by weight, dyes and bitter substances for reasons of hygiene and safety in the event of swallowing, for example of the denatonium benzoate type, as further conventional assistants.

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The present invention also relates to ready-to-use aqueous heat transfer liquids having a depressed freezing point and the use thereof in solar plants, which comprise water and from 10 to 90, in particular from 20 to 60, % by weight of the novel heat transfer concentrates.

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The novel heat transfer concentrates are distinguished not only by effective corrosion inhibition of the metals or alloys listed at the outset and good high-temperature stability but in particular additionally provide very good protection from glass corrosion in applications in modern solar plants in which the heat transfer liquid is in direct contact with the glass of the solar plant, for example the glass tubes.

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The example which follows illustrates the invention without restricting it.

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## Examples

The preparation of the novel heat transfer concentrates can be effected by mixing together the stated components, as described by way of example below for the novel concentrate 1.

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|  | Concentrate 1 | Comparative<br>concentrate A | Comparative<br>concentrate B |
|--|---------------|------------------------------|------------------------------|
|  | % by weight   | % by weight                  | % by weight                  |
| 1,2-Propylene glycol                                       | 94            | 94                           | 94                           |
| Polyacrylic acid (Sokalan® CP 10 S)                        | < 0.5         | <0.5                         | <0.5                         |
| Potassium hydroxide solution<br>(50% strength)             | < 0.3         | < 0.3                        | < 0.3                        |
| Tolutriazole   | < 0.2         | < 0.2                        | < 0.2                        |
| Benzotriazole  | < 0.1         | < 0.1                        | < 0.1                        |
| Sodium molybdate dihydrate                                 | < 0.1         | < 0.1                        | < 0.1                        |
| Hydroxyalkylamine  | < 5           | < 5                          | < 5                          |
| Antifoam (Pluriol® PE 10100)                               | 40 ppm        | 40 ppm                       | 40 ppm                       |
| Borax (sodium tetraborate · 10 H <sub>2</sub> O)           | ---           | ---                          | 0.20                         |
| Sodium metasilicate<br>(stabilized with silicophosphonate) | 0.20          | ---                          | ---                          |
| Water  | Remainder     | Remainder                    | Remainder                    |

1,2-Propylene glycol was initially taken, and polyacrylic acid, potassium hydroxide solution, tolutriazole, benzotriazole, sodium molybdate dihydrate, the hydroxyalkylamine and antifoam were added in succession while stirring at room temperature. After complete  
10 dissolution of all starting materials, the sodium metasilicate diluted beforehand in the ratio 1 : 9 with water and stabilized with silicophosphonate was added and stirring was carried out until a clear, homogeneous liquid was present.

The novel concentrate 1 thus obtained and the analogously prepared comparative  
15 concentrates A and B were diluted in the ratio 45 : 55 with water and tested as in example 1 according to the invention and as comparative examples A and B in the tests described below.

## A Glass corrosion

For the test, borosilicate glass ampoules (dimensions in mm: 14.75 x 0.55) are used. Each container is washed twice with distilled water and once with doubly distilled water. After drying for about 1 hour at 150°C, the ampoules are cooled to room temperature, cleaned on the outside with ethanol and weighed. The ampoules are then filled with 5.5 ml of test solution, closed with an aluminum foil and left for 24 hours at 135°C in an autoclave (type 112 from KSG Sterilisatoren GmbH, 82140 Olching, temperature regulation of the thermocouple directly in a test specimen in each case).

The containers are removed from the autoclave while taking the usual precautions and are cooled to room temperature in the course of one hour. The ampoules are emptied, washed about five times with distilled water, dried again for about one hour at 150°C, cooled and weighed.

The test results with example 1 according to the invention and comparative examples A and B are shown in table 1.

**Table 1:** Testing of the resistance of borosilicate glass

|               | Example 1             | Comp. example A       | Comp. example B       |
|---------------|-----------------------|-----------------------|-----------------------|
| Glass ampoule | Weight change<br>[mg] | Weight change<br>[mg] | Weight change<br>[mg] |
| 1             | + 0.1                 | - 0.1                 | - 0.1                 |
| 2             | + 0.1                 | - 0.2                 | - 0.3                 |
| 3             | + 0.1                 | - 0.2                 | - 0.3                 |
| 4             | + 0.2                 | - 0.2                 | - 0.3                 |
| 5             | + 0.2                 | - 0.1                 | - 0.3                 |
| 6             | + 0.2                 | - 0.3                 | - 0.4                 |
| 7             | + 0.1                 | - 0.2                 | - 0.3                 |
| 8             | + 0.1                 | 0                     | - 0.4                 |
| 9             | + 0.1                 | - 0.4                 | - 0.3                 |
| 10            | + 0.2                 | - 0.1                 | - 0.3                 |
| 11            | + 0.1                 | - 0.2                 | - 0.4                 |
| 12            | + 0.1                 | - 0.3                 | - 0.2                 |
| 13            | + 0.2                 | - 0.4                 | 0                     |
| 14            | + 0.1                 | - 0.2                 | - 0.3                 |



|                 | Example 1             | Comp. example A       | Comp. example B       |
|-----------------|-----------------------|-----------------------|-----------------------|
|                 | Weight change<br>[mg] | Weight change<br>[mg] | Weight change<br>[mg] |
| Glass ampoule   |                       |                       |                       |
| 15              | + 0.2                 | - 0.2                 | - 0.2                 |
| Ø weight change | + 0.1                 | - 0.2                 | - 0.3                 |
| pH before       | 9.7                   | 8.4                   | 9.7                   |
| pH after        | 9.7                   | 8.5                   | 9.6                   |

The results demonstrate that novel heat transfer liquids, such as example 1, have substantially improved glass corrosion prevention compared with the prior art (comparative example); in example 1, no weight loss was detectable in any of the 15 glass test specimens.

5 Comparative example B furthermore shows the corrosive effect of borates on glass.

#### B Glassware corrosion test according to ASTM D 1384-97

The results of the glassware corrosion test according to ASTM D 1384-97 furthermore demonstrate that the novel heat transfer liquids also protect metals from corrosion at least as well as the prior art.

Table 2 shows the test results

15 **Table 2:** Glassware corrosion test according to ASTM D 1384-97

|                | Example 1                              | Comp. example A                        | Comp. example B                        |
|----------------|--|--|--|
| Test specimen  | Weight change<br>[mg/cm <sup>2</sup> ] | Weight change<br>[mg/cm <sup>2</sup> ] | Weight change<br>[mg/cm <sup>2</sup> ] |
| Copper         | - 1.1                                  | - 0.7                                  | - 1.4                                  |
| Soft solder    | - 0.6                                  | - 0.9                                  | - 67.2                                 |
| Brass          | - 0.8                                  | - 1.0                                  | - 2.2                                  |
| Steel          | + 0.1                                  | - 0.3                                  | - 0.1                                  |
| Gray cast iron | + 0.6                                  | - 0.9                                  | - 0.6                                  |
| Cast aluminum  | + 0.9                                  | - 1.5                                  | - 1.9                                  |
| pH before      | 9.7                                    | 8.4                                    | 9.7                                    |
| pH after       | 9.6                                    | 8.6                                    | 9.2                                    |